

Synthesis and characterization of GAP-based mesoporous energetic polymers

Guoping Li, Haoxue Dong, Menghui Liu, Min Xia¹, Chunpeng Chai, Yunjun Luo²

¹School of Materials and Science, Beijing Institute of Technology, Beijing100081, China. Tel./Fax: +86-10-68911608; E-mails: xminbit@bit.edu.cn (M.X.)

²School of Materials and Science, Beijing Institute of Technology, Beijing100081, China. Tel./Fax: +86-10-68913698; E-mails: yjluo@bit.edu.cn (Y.L.)

Mesoporous materials have high specific surface area and chemical stability, as well as unique light organic framework^[1]. Mesoporous energetic polymers combining mesoporous materials and energetic polymers, have the excellent properties of mesoporous materials and unique advantages in controllability and safety of energy output, energy release and so on. In this paper, macroinitiator GAP-Br, with a hydroxyl content of 54% and a

bromo group content of 46%, was obtained by using polyazide glycidyl ether (GAP, $\overline{M}_n=4000$, functionality=2.1) as precursor to react with 2-bromoisobutyryl bromide in the presence of 4-dimethylaminopyridine (DMAP) and was characterized by Fourier transform infrared spectroscopy (FTIR), nuclear magnetic proton (¹H NMR) and gel permeation chromatography (GPC).

GAP-PS diblock copolymer was synthesized by initiating the polymerization of styrene with macroinitiator GAP-Br through the atom transfer radical polymerization (ATRP). GPC showed the number-average molecular weight of GAP-PS was 6000-8000 and its polymer dispersity index (PDI) was 1.13-1.37.

Using stannous octoate as a catalyst, PLA-GAP-PS was prepared by the copolymerization of GAP-PS and lactide through the coordination-insertion polymerization. The number-average molecular weight of products was 8000-10000 and the PDI was 1.20-1.40. The excessive amount of stannous octoate would cause the decomposition of azide group and the reaction time should be controlled in 25-30 h.

PLA-GAP-PS micelles, which were like three layers of the onion, were obtained by self-assembly in toluene. When the concentration of micelles was 5 mg/ml, the size of them was about 50 nm; when the concentration was 10 mg/ml, the size was about 100 nm; when the concentration was 15 mg/ml, the size was about 250 nm.

The self-assembled micelles were soaked in lye to degrade PLA chains and mesoporous energetic polymers with controlled mesoporous were prepared. The polymerization degree of PLA segments and the concentration of PLA-GAP-PS affected the morphology and size of micelles obtained by self-assembling the triblock copolymer, thus affecting the density and diameters of mesoporous of PLA-GAP-PS triblock polymer micelles after etching. In the meanwhile, the self-assembly concentration and the residual amount of toluene when adding lye affected the subsequent precipitation process, and further affected the mesoporous morphology, size and density. When the self-assembly concentration was 5mg/ml, the pore density was the largest. The pore diameter was higher, the morphology was more rounded and the density was lower with more residual amount of toluene. The addition of accelerator (sodium dodecyl sulfate) could improve the composition of the etching solution and promote the wetting process^[2], so that the morphology of mesoporous was more regular and the density was higher. Etching time and temperature would affect the degree of etching reaction. The longer the etching time was, the more complete the etching reaction was and the larger the density was. The reaction was basically complete in 10 days and the optimal temperature was about 50°C. When the etching temperature was low, the etching rate was low, the etching reaction was incomplete and the pore density was small. When the temperature was high, it would affect the glass transition temperature of the nanoporous skeleton^[3], with the samples' surface becoming uneven.

Keywords mesoporous energetic polymers; ATRP; self-assembly

References

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